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Dated 18 JUL 2000

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The  
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Oct 1977

THE PATENT OFFICE

25 SEP 1999

# Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

1. Your reference

BKCD/NS/DBN.106

2. Patent applicant  
(The Patent Office)

9922691.2

25 SEP 1999

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Trikon Holdings Limited  
Coed Rhedyn  
Ringland Way  
Newport  
Gwent  
NP6 2TA

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

743 5423001

4. Title of the invention

Delivery of Liquid Precursors to  
Semiconductor Processing Reactors.

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom  
to which all correspondence should be sent  
(including the postcode)

Wynne-Jones, Laine & James  
22 Rodney Road  
Cheltenham  
GL50 1JJ

Patents ADP number (if you know it)

1792001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

Yes

- a) any applicant named in part 3 is not an inventor, or
  - b) there is an inventor who is not named as an applicant, or
  - c) any named applicant is a corporate body.
- See note (d))

# Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description 10

Claim(s) 2

Abstract 0

Drawing(s) 34/18

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77) 1

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11. I/We request the grant of a patent on the basis of this application.

Signature

Date

Wynne Jones Laine & James

24.9.99

12. Name and daytime telephone number of person to contact in the United Kingdom

Mr. B. Dunlop

01242 515807

## Warning

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## Notes

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Delivery of Liquid Precursors to Semiconductor

Processing Reactors

This invention relates to methods and apparatus for delivering liquid precursors to semiconductor processing reactors.

There is a good discussion of various prior art proposals for delivering such precursors in the preamble of United States Patent 5620524 and the reader is referred to this. In general a liquid precursor will be a gas at the low pressures, which typically exist in the reactor (e.g. 1 torr), but at atmospheric pressure (15 torr) they will be in their liquid state. This gives rise to practical delivery and measurement problems, which are exacerbated by the highly reactive nature of many of these precursors, which limit the choice of engineering materials that may be used. Most liquid precursor delivery systems, which are used in wafer processing, are of one of the following three types:

1. There is vaporisation of the liquid and the use of a gas mass flow controller.
2. Use of a liquid mass flow controller.
3. A carrier gas is passed through a liquid in a "bubbler" to vaporise some of the liquid in the carrier gas bubbles.

Whilst gas mass flow measuring instruments are widely used, they present problems when the liquid has to be vaporised for mass flow measurement. A large reservoir of vaporised liquid is required, which increases the residence time of the vaporised liquid at a raised temperature. For peroxide, which is a useful precursor, decomposition may commence before it reaches the process chamber. Liquid mass flow controllers are capable of giving good flow control but are liable to instabilities, believed to be caused by bubbles forming in the mass flow controller whilst in its idle state and the cold liquid cooling the controller can cause calibration drift. Bubblers require a carrier gas and the lower the vapour pressure, the less liquid that is taken up as vapour by the bubbles. Therefore, for low vapour pressure liquids, a high flow of carrier gas is required and that may be incompatible with the process.

As alternatives to these approaches, an arrangement similar to that shown in US 5620524 has been tried comprising a positive displacement pump in combination with a narrow bore outlet pipe, but as well as difficulties in selecting appropriate materials for such pumps and other parts, flow variations are experienced due to variations in bore of the narrow bore pipe, necessary

to buffer the low pressure chamber from the pump. Such arrangements are susceptible to variations because the flow restriction of the narrow bore pipe dominates as the pump is essentially a pressurisation device, flow being  
5 determined by pressure. The method is referred to as "standard" in Figure 4 below.

A simpler version of this system can be used if a pre-set or fixed flow is acceptable. The system then entirely depends on the action of ambient pressure upon  
10 the liquid to replace the use of the pump and the flow restricting tubing to control flow. This system makes use of the fact that clean rooms are pressure controlled environments at slightly above atmospheric pressure. The system is still however dependent on the internal bore  
15 diameter of the pipe being accurate and in suitably compatible materials this is not often the case. Specific system calibration can therefore become necessary and different pipe lengths may need to be used depending on the actual bore diameter.

20 US Patent 5620524 describes an alternative using out-of-phase piston pumps, but it relies on the system knowing various characteristics of the precursor and monitoring the temperature and pressure of the precursor in order to deliver a desired mass of precursor.

From one aspect the invention consists in apparatus for delivering a liquid precursor to a semiconductor processing reactor comprising a source of a liquid precursor, a volume calibrated positive displacement pump drawing liquid precursor from the source via an input path and for delivering, along an output path, a known volume of liquid precursor to the reactor. Either just prior to the reactor or within the reactor the liquid precursor may be evaporated, for example by a flash evaporator.

The apparatus may further include a valve for connecting the pump to the input path or the output path. The apparatus may further comprise control means for controlling the pump and the valve whereby the pump draws liquid in, whilst the reactor is not processing with this precursor. Additionally or alternatively the apparatus may further include control means for controlling the pump and the valve whereby the pump returns any undelivered precursor to the source.

The pump may be in the form of a syringe pump.

The source may include another reservoir of liquid precursor and preferably the source may include at least two bottles or reservoirs and means for automatically connecting one bottle or reservoir to the inlet path as the other becomes empty.



From another aspect the invention consists in a method of delivering a liquid precursor to a semiconductor processing reactor including:

1. A liquid precursor, along an input path, into a volume calibrated positive displacement pump from a source of liquid precursor;
2. Delivering, along an output path, a known volume of liquid precursor to the reactor.

The liquid precursor may be evaporated either just before it reaches the reactor or within the reactor.

This may further include permanently connecting the pump to the input path and the output path. Additionally or alternatively, after each volume delivery, the pump may return any remaining liquid to the source, before drawing a fresh charge.

Although the invention has been defined above it is to be understood it includes any inventive combination of the features set out above or in the following description.

The invention may be performed in various ways and specific embodiments will now be described, by way of example, with reference to the accompanying drawing in which:

Figure 1 is a schematic view of a liquid precursor delivery system;

Figure 2 is a graph indicating flow rate from the system; and

5        Figure 3 is a further graph indicating variations in deposition rates using a variety of liquid precursor delivery systems.

10        A liquid precursor delivery system is generally indicated at 10 in Figure 1. The system 10 includes a precursor source generally indicated at 11, an inlet tube 12, a two-way valve 13, a pump assembly, generally indicated at 14, an outlet tube 15, a shut off valve 16, and a flash evaporator 17.

15        The liquid precursor source 11 comprises a pair of bottles 18, 19 contained within a temperature controlled chamber 20, level sensors, schematically indicated at 21 detect the level of liquid in the respective bottles 18, 19. The bottles 18, 19 are connected to a valve 22 and thence to the inlet tube 12. The valve 22 is arranged to  
20        connect one or other of the bottles 18, 19 to the tube 12.

      The pump assembly 14 is of the type generally known as a syringe or variable volume pump, such as, for example, made by Lee Products in their LPV series. Such pumps have a syringe 24 comprising a tube 25 and a piston

26. The piston is linked to a stepper motor 27 and in general means are provided for detecting the linear movement of the piston to determine the volume of liquid expelled from the syringe.

5 In the illustrated arrangement the stepper motor 27 drives a lead screw 28 which in turn linearly moves a carriage 29 that is connected to the free end of the piston 26. The linear position of the carriage 29 is detected by a linear encoder 30. As the position of the carriage 29 is revealed very precisely by the linear encoder 30, the position of the piston 26, and hence the volume of liquid displaced, can be very tightly controlled. Further the whole arrangement enables liquid to be expelled at high pressure.

10 The pump assembly 14 and valves 13, 16 and 22 are all under the control of a control circuit 31, which is in turn responsive to the linear encoder 30 and the level sensors 21, as well as other processing information from the associated reactor.

15 In use the stepper motor 27 initially draws the carriage 29 in a downward direction, which moves the piston in a withdrawing sense within the tube 25. With the valve 13 set to connect the pump 24 to the liquid source 11, the liquid precursor can be drawn from one or

other of the bottles 18, 19 depending on the position of the valve 22. Once the pump 24 is charged, the stepper motor 27 stops. The valve 13 is then switched to connect the syringe pump 24 to the outlet tube 15 and at the right moment, in processing, the shut off valve 16 is opened and the stepper motor reverses the motion to drive the piston 26 back within the tube 25 causing liquid precursor to be delivered into the flash evaporator 17. The volume of liquid expelled is directly related to the travel of the piston 26 and hence of the carriage 29. This can be monitored by the control circuit 31 via the linear encoder 30 and as soon as the desired volume is achieved, the stepper motor 27 is turned off. Thus it will be seen that very precise volumes of liquid precursor can be delivered at high pressure into the evaporator without the problems which arise with other systems.

It is preferred that the syringe is filled with more than the required volume to prevent any shortage in delivery. Conveniently, then the unexpelled liquid can be returned to the bottles 18, 19 via a valve 13, tube 12 and valve 23 so that the liquid precursor can be kept in the best conditions possible.

The provision of two bottles enables one bottle to be switched over when it becomes empty, without any interruption in processing being necessary.

It is thus anticipated that wafers or batches of wafers can be introduced into the reactor chamber, a precise volume of liquid precursor delivered into the chamber via the flash evaporator 17 and thereafter the pump can be emptied and recharged ready for the next wafer or batch.

Figure 2 illustrates the linearity in flow rate that can be achieved with the system of the invention and hence the accuracy of volume delivery.

Figure 3 illustrates the resultant benefits in terms of repeatability deposition rate. It will be seen that the syringe produces a very repeatable level of deposition using a hydrogen peroxide system as compared with earlier delivery proposals.

The system has a number of advantages:

1. It can be self primed at the beginning of a run and hence clear any lines of degraded hydrogen peroxide and bubbles from the line and syringe.
2. The syringe need only be filled immediately prior to the process avoiding degradation of the liquid precursor.
3. The delivery rate can be fully programmable.

4. The delivery rate can be fully monitored by the linear encoder.

5. Any excess liquid precursor is returned to the source at the end of the process.

5 6. Continuous running through the automatic bottle changeover can be easily achieved. These benefits have been particularly noted with such precursors as hydrogen peroxide which do tend to degrade when not kept under suitable conditions. The delivery system also works very well with hydrogen peroxide being accurate to below 1 gram per minute. Flow rates can be easily changed without any significant loss of accuracy simply by changing the pump tubes and the matching pistons.

10  
15 Experiments, which are reported, in our copending application entitled "Method and Apparatus for forming a film on a substrate" using conventional systems and then a syringe pump to deliver cyclohexyldimethoxymethylsilane show that for at least some precursors and processes acceptable results are only obtained when a syringe pump assembly as described is used. This disclosure is  
20 incorporated herein by reference.

CLAIMS

1. Apparatus for delivering a liquid precursor to a semiconductor processing reactor including a source for the liquid precursor, a volume calibrated positive displacement pump for drawing liquid precursor from the source via an input path and for delivering along an output path a known volume of liquid precursor to the reactor.

2. Apparatus as claimed in Claim 1 further including a valve for connecting the pump to the input path or the output path.

3. Apparatus as claimed in Claim 2 further including control means for controlling the pump and valve whereby the pump draws liquid in, whilst the reactor is not processing with this precursor.

4. Apparatus as claimed in Claim 2 or Claim 3 further including control means for controlling the pump and the valve whereby the pump returns any undelivered precursor to the source.

5. Apparatus as claimed in any one of the preceding claims wherein the pump is a syringe pump.

6. Apparatus as claimed in any of the preceding claims wherein the source includes a bottle or reservoir of liquid precursor.

7. Apparatus as claimed in Claim 6 wherein the source includes at least two bottles or reservoirs and means for automatically connecting one bottle or reservoir to the inlet path as the other becomes empty.

5 8. A method of delivering a liquid precursor to a semiconductor processing reactor including:

(i) Drawing a liquid precursor along an input path, into a volume calibrated positive displacement pump from a source of liquid precursor; and

10 (ii) Delivering, along an output path, a known volume of liquid precursor.

9. A method as claimed in Claim 8 including alternately connecting the pump to the input path and the output path.

10. A method as claimed in Claim 8 or Claim 9 wherein  
15 after each volume delivery the pump returns any remaining liquid to the source, before drawing a fresh charge.



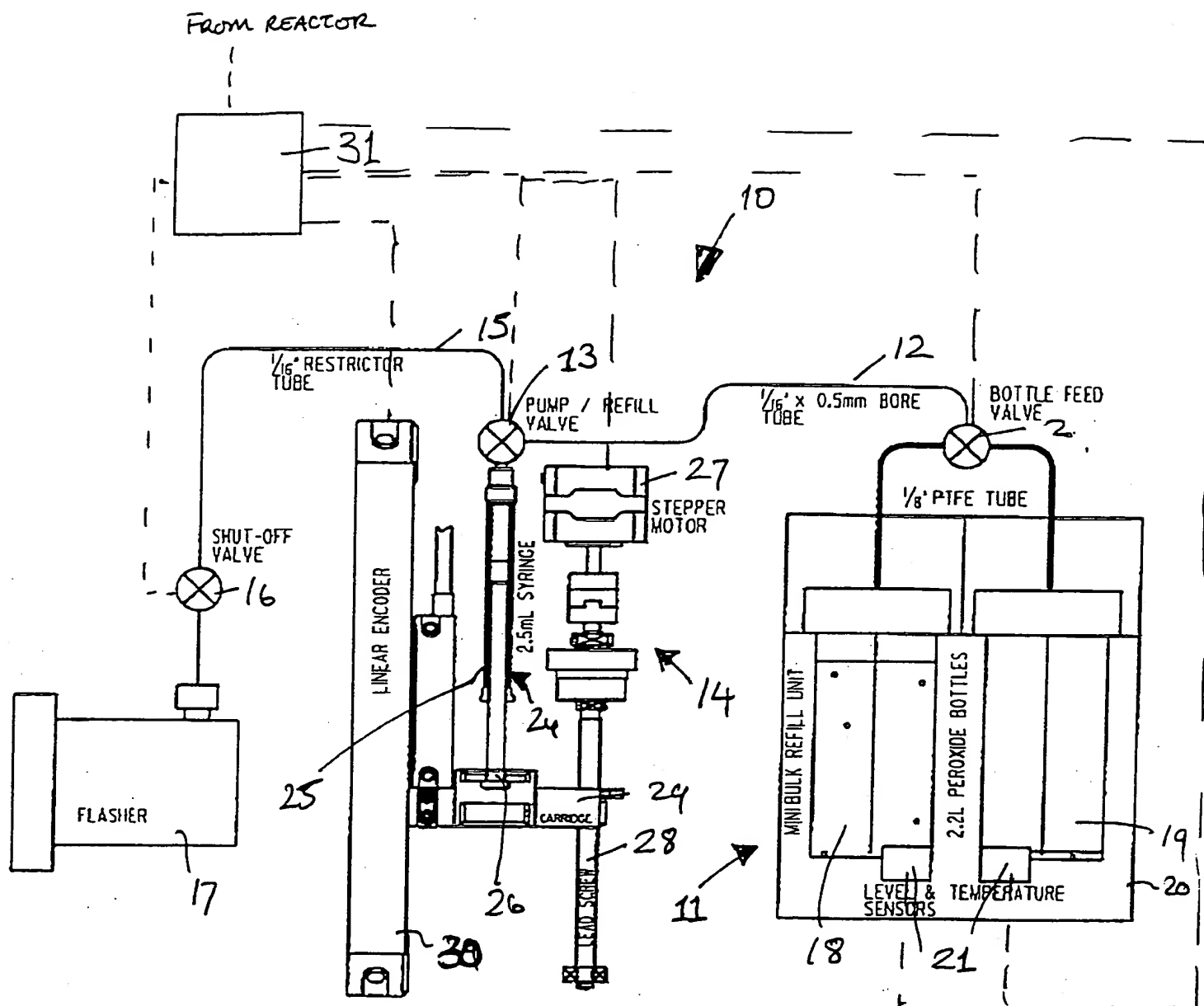


FIG 1.

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**Injection System**  
**(onto Balance at Atmosphere)**

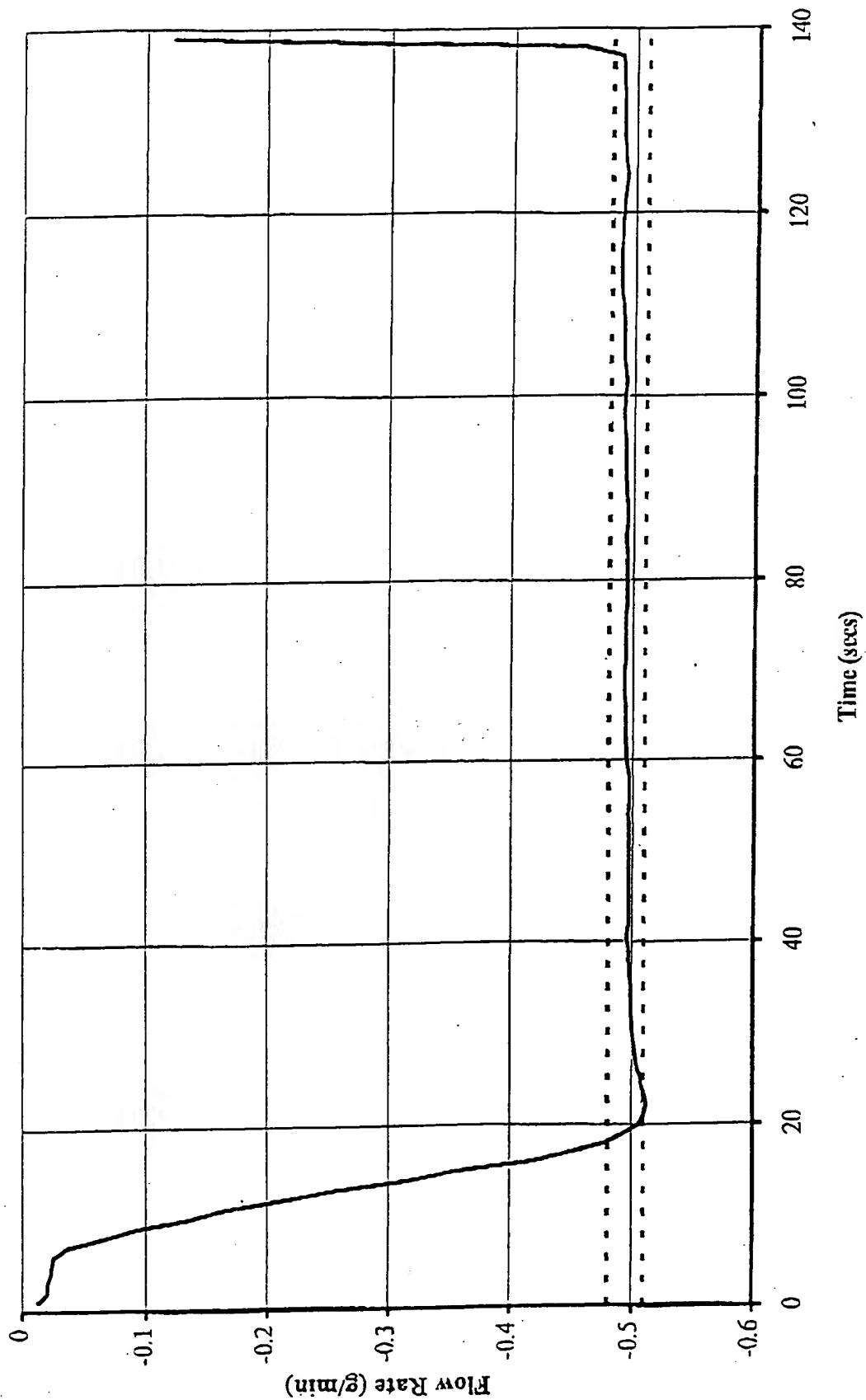


FIG 2

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# Hydrogen Peroxide Delivery System ET2 Process

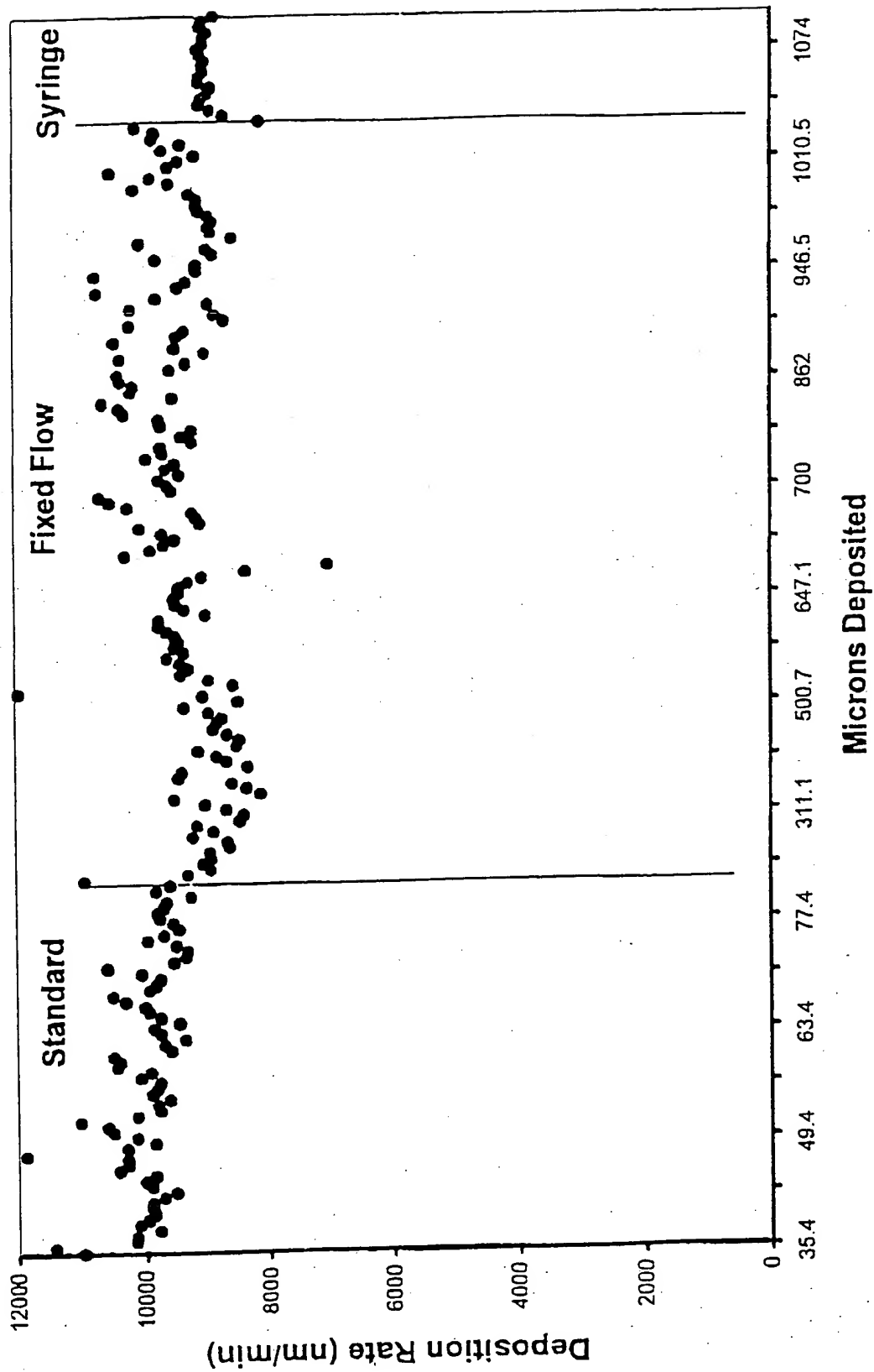


FIG 3.

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Wynne Jones (a)ne a James